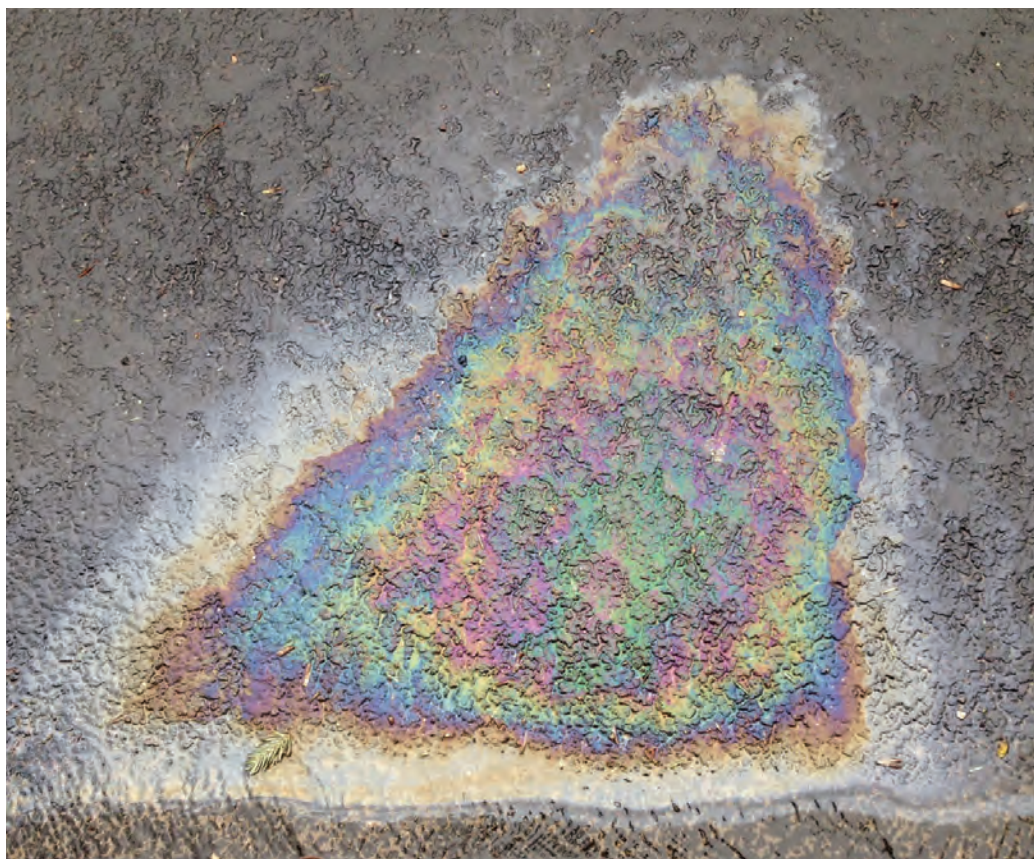


Royal Society of Chemistry Environmental Chemistry Group

([www.rsc.org/ecg](http://www.rsc.org/ecg))

January 2015

# ECG *Bulletin*



**We are celebrating!** Twenty years ago, the first issue of this publication, then called the *ECG Newsletter*, was published. For this anniversary, we are taking an opportunity to look back at some past issues of the *ECG Bulletin* and to review some of the topics that have engaged those who teach and research into environmental chemistry in the UK (pages 4-12).

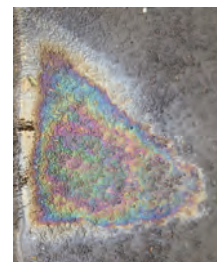
**Threats to avian predators.** Avian predators such as vultures are under

threat in Africa and Europe, both from deliberate poisoning and from veterinary agents in carcasses that they feed on. Read more on page 17.

**Environmental Briefs.** We continue our series of concise environmental chemistry primers with Briefs on how to calculate atmospheric lifetimes of trace gases (page 21) and on measuring NO<sub>2</sub> concentrations (page 23).

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*Oily water on a London Street*

## ECG Bulletin

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# Chairman's report for 2014

James Lymer (Wardell Armstrong)

During 2014, the Environmental Chemistry Group committee organised a number of successful meetings, events and activities across a range of topics and formats, in some cases jointly with other interest groups, and organisations.

In February, the ECG and the RSC Toxicology Group jointly arranged an event on **Organic Chemistry and Toxicity of Contaminants in the Ground**. At this one-day meeting, about 54 delegates heard presentations from seven speakers on topics including *Emerging organic groundwater contaminants and their transformation products* by Marianne Stuart (BGS), *Side Effects of Medication in the Soil Environment* by Prof. Alistair Boxall (University of York) and *The Environmental Fate Simulator: a tool for predicting the degradation pathways of organic chemicals in groundwater aquifers* by Dr Eric J. Weber (US EPA). A meeting report appeared in the July 2014 edition of the *ECG Bulletin*.

This meeting was followed by the 2014 Distinguished Guest Lecture and Symposium on 12th March, on the topic of **Plastic debris in the ocean – a global environmental problem**. The speakers were Prof. Norman Billingham (University of Sussex, *Polymers and their environmental degradation*), Dr Edwin Foekema (IMARES, *Aspects that determine the actual risk of plastic associated POPs for marine organisms*), and Dr Heather Leslie (VU University, *Macroplastics and Microplastics – what is their environment impact?*). The Distinguished Guest Lecture was delivered by Prof. Richard Thompson of Plymouth University, who spoke to the symposium title. Detailed reports can be found in the July 2014 edition of the *ECG Bulletin*. About 48 delegates attended the meeting.

On 10th December, the ECG and the Molecular Physics Group of the Institute of Physics (IOP) co-organised a meeting on **Soft ionisation mass spectrometric techniques and the environmental sciences** at the University of Birmingham. This half-day meeting followed on from the successful meetings on this subject area in recent years and was attended by 36 delegates, with talks from Prof. Thomas Karl (University of Innsbruck, Austria), Dr Rachael Beale (Plymouth Marine Laboratory), Dr Gavin Phillips (University of Chester); and Dr Markus Kalberer (University of Cambridge).

Alongside our programme of events, ECG Committee members Julia Fahrenkamp-Uppenbrink, Roger Reeve,

Rowena Fletcher-Wood and Cecilia Fenech have continued to produce the biannual **ECG Bulletin**. A revised format of the *ECG Bulletin* was introduced for this year's July edition. Dr Martin King (Royal Holloway) has been active in the further development of the **ECG Environmental Briefs**, a series of short documents giving a brief but precise introduction to topics of relevance to environmental chemistry. ECG Environmental Briefs on *Atmospheric chemistry at night*, *Atmospheric particulate matter*, *Asbestos in soils* and *Pourbaix (pE-pH) diagrams for the aquatic environment* were published in the January and July 2014 editions, respectively. Further Briefs appear on pages 21 and 23 of this issue. The Briefs also have a dedicated web page on the ECG Group website ([www.rsc.org/Membership/Networking/InterestGroups/Environmental/index.asp](http://www.rsc.org/Membership/Networking/InterestGroups/Environmental/index.asp)).

Forthcoming events in 2015 include **New developments in the analysis of complex environmental matrices**, a one-day meeting to be held at Burlington House on 6th February 2015 (see page 13), and **Emerging contaminants in waters and soils, practical considerations: sampling, analysis and consequences**, a one-day meeting to be held at The Source, Sheffield on 4th March 2015 (see page 20). The **2015 ECG DGL and Symposium** will be held on 24th June 2015, at Burlington House. The topic for this event is 'Nanomaterials: environmental remediants or toxicants?', and the **2015 Distinguished Guest Lecturer** will be **Professor Éva Valsami-Jones** (Professor of Environmental Nanoscience at Birmingham University). Booking and programme information will be sent out soon to all ECG members.

The committee is always keen to hear from members, including feedback on events, suggestions for future activities, and other ideas, and we look forward to seeing you in 2015.

The Environmental Chemistry Group held its 40th Annual General Meeting in 2013, while 2015 sees the twentieth anniversary since the first edition of the *ECG Bulletin* (formerly the *ECG Newsletter*), an anniversary that we are celebrating with a set of articles in this issue (see pages 4 to 12). The Group's membership has grown to around 2,000 members. The Group has a long history of bringing activities to the membership and the wider community which I am sure will continue well into the future. I thank the committee and those who have participated in the diverse activities of ECG for volunteering their time.

Anniversary article

# ECG Newsletter and ECG Bulletin, January 1995 – January 2015

Rupert Purchase (Haywards Heath, rp@rupertpurchase.demon.co.uk)

The ECG *Newsletter* was first published for members of the RSC's Environmental Chemistry Group (ECG) in January 1995, and renamed (for reasons the author can no longer remember) the ECG *Bulletin* in 2002. This twentieth anniversary issue provides a good opportunity to reiterate the rationale for providing this biannual publication and to review some of the content of the past forty editions.

In 1994, the 'Environment Group' (inaugurated in 1972 and later affiliated to the RSC's Industrial Division) was renamed the 'Environmental Chemistry Group' (affiliated to the RSC's Scientific Affairs Board). The first issue of the ECG *Newsletter* (Figure 1) explained this decision and its implications. Also in that issue, a long-serving committee member and a past Chair and Treasurer, Geoff Dickes, reviewed the history of the Environment Group and some of the scientific meetings the Group had organised during the previous twenty years. These included the ECG Distinguished Guest Lecture (DGL), which remains a pivotal day in the Group's scientific profile.

From its inception, the publication has had a number of objectives:

- To summarise recent meetings organised by the ECG, and meetings with an environmental chemistry theme hosted by similar organisations;
- To give details of forthcoming ECG meetings and other symposia in environmental chemistry;
- To provide a platform for newly-qualified PhD students to review their research into the environmental sciences;
- To describe the teaching of environmental chemistry in the UK and in Europe;
- And to allow those with a specialised knowledge, interest or concern an opportunity to review a particular topic in the environmental sciences.

Other features in the publication have included book reviews and details of books on the environment, toxicology, and health and safety acquired by the RSC

Library and Information Centre.

In 2009, Dr Adrian Kybett redesigned the ECG *Bulletin* and it acquired an International Standard Serial Number (ISSN). Printed copies of the ECG *Bulletin* from 2002 onwards are available at the British Library in the St Pancras Reading Rooms, London; two copies of each edition are held by the RSC Library at Burlington House.

Because of increased costs of producing and distributing printed copies of the ECG *Bulletin*, the publication has only been available to members as an electronic version from July 2012 onwards. A few printed copies are still produced to publicise the ECG and to donate to the British and RSC Libraries. All copies of the ECG *Newsletter* and ECG *Bulletin* are available online without cost or registration at [www.rsc.org/Membership/Networking/InterestGroups/Environmental/ECGBulletin.asp](http://www.rsc.org/Membership/Networking/InterestGroups/Environmental/ECGBulletin.asp). Further improvements to the design by the current editor Dr Julia Fahrenkamp-Uppenbrink allow quicker access to individual articles and features in

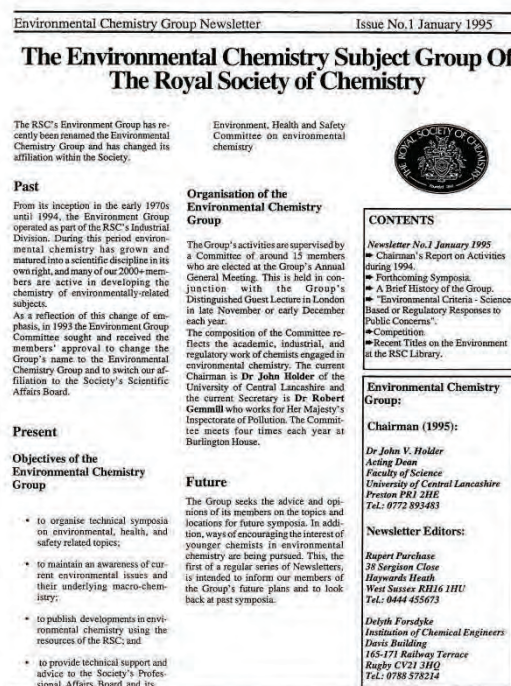


Figure 1. The front page of the first edition of the ECG Newsletter, published in January 1995.

the web version.

What have been some of the highlights of the past twenty years? In June 1998, we featured the first of two contributions by ECG member Michael Brooks on the contamination of drinking water by arsenic in Bangladesh and some available technologies for the removal of this carcinogenic and toxic metalloid. Other articles on arsenic followed, discussing its occurrence in other countries, mechanisms of toxicity, and arsenic speciation (see for example the July 2004 and January

2006 editions). Over the past decade, Professor John McArthur and his colleagues at the Department of Earth Sciences, UCL have unravelled some of the geochemical factors, which lead to arsenic contamination in drinking water, as John McArthur explained in three issues (January 1999, January 2009 and September 2011).

Research associated with climate change and its implications for human habitation is perhaps of most interest for those who follow scientific developments, and the ECG has tried to reflect this interest in a

**Table 1:** *Honorary RSC Environmental Chemistry Group Officers, 1995–2015*

<b>Year</b>	<b>Chair</b>	<b>Vice-Chair</b>	<b>Secretary</b>	<b>Treasurer</b>
1994–1996	Dr John Holder University of Central Lancashire	Professor C. Nicolas Hewitt Lancaster University	Dr Robert Gemmill HMIP, Bristol	Dr Peter O'Neill University of Plymouth
1996–1997	Professor C. Nicolas Hewitt	Dr John Holder	Dr Mike E. Jenkin AEA Technology, Abingdon	Dr Peter O'Neill
1997–1998	Professor C. Nicolas Hewitt	Dr Peter O'Neill	Dr Leo Salter Cornwall College, Redruth	Dr Trevor Pryce-Jones† University of Hertfordshire
1998–1999	Dr Peter O'Neill	Professor C. Nicolas Hewitt	Dr Leo Salter	Dr Trevor Pryce-Jones†
1999–2000	Dr Peter O'Neill	Dr Leo Salter	Dr Andrea Stroh University of Leeds	Dr Trevor Pryce-Jones†
2000–2001	Dr Leo Salter	Dr Peter O'Neill	Dr Andrea Stroh	Professor Peter Craig De Montfort University
2001–2002	Dr Leo Salter	Dr Andrea Jackson (née Stroh) University of Leeds	Dr Rob MacKenzie Lancaster University	Dr Brendan Keely University of York
2002–2003	Dr Andrea Jackson	Dr Leo Salter	Dr Rob MacKenzie	Dr Brendan Keely
2003–2004	Dr Andrea Jackson	Dr Brendan Keely	Dr Leo Salter	Dr Brendan Keely
2004–2005	Dr Brendan Keely	Dr Andrea Jackson	Dr Leo Salter	Dr Andrea Jackson
2005–2007	Dr Brendan Keely	Dr Andrea Jackson	Jo Barnes Cornwall College, Redruth	Dr Andrea Jackson
2007–2008	Dr Brendan Keely	Dr Andrea Jackson	Jo Barnes	Dr Ruben Sakrabani Cranfield University
2008–2009	Dr Brendan Keely	Dr Leo Salter	Jo Barnes University of West England	Dr Ruben Sakrabani
2009–2010	Dr Leo Salter	Dr Brendan Keely	Jo Barnes	Dr Ruben Sakrabani
2010–2011	Dr Leo Salter	Dr William Bloss University of Birmingham	Jo Barnes	Dr Ruben Sakrabani
2011–2012	Dr Leo Salter	Dr William Bloss	James Lymer Wardell Armstrong LLP, Sheffield	Jo Barnes
2012–2013	Dr William Bloss	Dr Leo Salter	James Lymer	Jo Barnes
2013–2014	Dr William Bloss	James Lymer	Dr Martin King Royal Holloway, University of London	Jo Barnes
2014–2015	James Lymer	Dr William Bloss	Dr Martin King	Dr Jo Barnes

The names of institutions and the authors' affiliations may have changed since the dates indicated.

**Table 2:** *ECG Newsletter and ECG Bulletin Editors, 1995-2015*

1995	Rupert Purchase, Delyth Forsdyke
1996	Rupert Purchase, Meg Heaton, Delyth Forsdyke
1997–2005	Rupert Purchase
2006–2008	Rupert Purchase, Ruben Sakrabani, Jo Barnes
2009–2011	Rupert Purchase, Adrian Kybett, Ruben Sakrabani, Roger Reeve
2011	Rupert Purchase, Cecilia MacLeod, Roger Reeve
2012–2013	Julia Fahrenkamp-Uppenbrink, Rupert Purchase, Roger Reeve
2014–	Julia Fahrenkamp-Uppenbrink, Roger Reeve, Rowena Fletcher-Wood

measured and balanced way. Four articles on climate change arising from an ECG DGL and Symposium, *Climate Change and its Impact*, organised at the start of this millennium, were published in the July 2000 issue, including an article by Sir John Houghton on the likely impacts of climate change. Fifteen years later the relevance of these articles is still apparent.

Over the years, the ECG Distinguished Guest Lecture and accompanying symposium, held usually in March each year in London, has provided plenty of informative copy for the *ECG Bulletin*. Titles of past ECG DGLs from 1986 onwards may be found at [http://www.rsc.org/images/The-ECGs-Distinguished-Guest-Lecturers-2014\\_tcm18-185778.pdf](http://www.rsc.org/images/The-ECGs-Distinguished-Guest-Lecturers-2014_tcm18-185778.pdf). Speakers at these events are invariably very willing to write for the *ECG Bulletin*. The Group has also benefitted for many years from Leo Salter's detailed and fluent written summaries of the day's proceedings.

Changes in the composition of the ECG committee are reflected in other topics selected for publication, notably atmospheric chemistry and environmental chemistry in the Arctic and Antarctic regions. Committee members and atmospheric chemists, Dr William Bloss and Dr Stephen Ball have reviewed their work in atmospheric halogen chemistry (*ECG Bulletin*, July 2009) as well as providing detailed summaries of the ECG Atmospheric and Environmental Chemistry Forums, which they have organised for early career researchers over the past few years (see, for example, *ECG Bulletin*,

February 2013). ECG member Professor Eric Wolff, FRS from the British Antarctic Survey was the main speaker for the ECG DGL and Symposium in 2007 ('Environmental chemistry in the Polar Regions'), and his talk on polar ice cores featured in the *ECG Bulletin*, July 2007 together with contributions from the other speakers at this event.

Two articles have highlighted concerns about the environmental effects of xenobiotics. Professors Elizabeth Hill and Charles Tyler reviewed their work on the identification of endocrine disruptors in wastewater outlets (*ECG Bulletin*, January 2005), and long-standing ECG committee member and *ECG Bulletin* Editor Dr Roger Reeve described some techniques used to remove pharmaceutical compounds found in sewage treatment works (*ECG Bulletin*, January 2010).

This brief survey of the past twenty years cannot list every contributor to the *ECG Newsletter* and *ECG Bulletin*. But perhaps we can conclude by mentioning the proceedings of a joint ECG and RSC Historical Group Symposium, which were published in the *ECG Bulletin*, January 2012. 'Environmental chemistry: a historical perspective' highlighted some of the scientists who first raised concerns about man's impact on the environment and laid the foundation of environmental chemistry as a distinct scientific discipline.

We hope that the *ECG Bulletin* will continue to flourish. Ideas and unsolicited contributions are always welcome. Please contact the *ECG Bulletin* Editors at [ecgbulletin@hotmail.co.uk](mailto:ecgbulletin@hotmail.co.uk) for advice.



**The ECG committee in December 2014 at Burlington House.** Front row: Zoë Fleming, Rowena Fletcher-Wood, Julia Fahrenkamp-Uppenbrink; middle row, Jo Barnes, Tom Sizmour, Bill Bloss, Martin King; back row, Steve Leharne, Ian Forber, Rupert Purchase, Roger Reeve, James Lymer.

## Anniversary article

# Environmental chemistry: a twenty year perspective

Leo Salter (Cornwall), James Lymer (Wardell Armstrong), Jo Barnes (University of the West of England), Cecilia Fenech (Cranfield University) and Ian Forber (ALcontrol Laboratories)

As part of the ECG *Bulletin's* twentieth anniversary edition, committee members reflect on the past and present of soil, air, and water quality management in the UK.

## Introduction

During the 20th and 21st centuries, society became a function of capitalist ideologies. As a consequence of this, consumerism is now a dominant and ubiquitous paradigm. If this is true, and since there is no altruism or aesthetic in capitalism, damage to the environment only becomes relevant when it impinges on profit. In my view this can occur in two ways, either as a collateral effect of the profit motive when a damaging action reduces profitability (e.g. when a commodity such as water or oil becomes so scarce/expensive that consumption is reduced) or when government is provoked (e.g. by popular action) to introduce legislation. In relation to the latter, it is noteworthy that in capitalist societies, many aspects of environmental legislation are justified economically, most often based on human health arguments constructed around the costs to the state of reduced economic activity and/or costs to national health systems. Legislation outside of these two categories is hard-won.

Arguments about the value, aesthetics, and long-term significance of the environment that cannot be couched in terms of economic value (profit) rarely attract the genuine commitment of governments. Without effective legislation by government, the preservation of the environment becomes a romantic and futile notion. In other words, legislation is currently the only tool at humanity's disposal that offers a route by which the complexity and wonder of the natural world can be preserved; the introduction and implementation of environmental legislation is vital.

I hope this personal view of the world we live in will suffice to introduce three brief surveys of the state-of-play of environmental legislation with regard to land, air and water in the UK and EC; readers may draw their own conclusions about its effectiveness and whether it will suffice.

**Leo Salter**

## Contaminated land management

In the UK, throughout late industrial and post-industrial society, legislation began to reflect the need to protect human health and the environment from pollution leading to a landmark regulation with the 1990 Environmental Protection Act (EPA). New policy initiatives and various pieces of specific legislation were introduced following enactment of the EPA.

Prior to the EPA, and with respect to soils and contaminated land, the Inter-Departmental Committee for the Development of Contaminated Land (ICRCL, formed in 1976) provided various Guidance Notes on land contamination. These included (a) advice to Local Authorities against development on landfill sites, (b) guidance on asbestos (1990) (c) trigger and intervention values for soil contaminants (1987) (to compare with site concentrations) as part of an emerging, risk-based assessment practice that had developed over the previous twenty years.



Following explosions in buildings on sites during the 1980s, where ground gas accumulation was identified as the source, technical guidance was introduced. Establishing ground gas conditions over the past twenty years has become a common feature of land redevelopment.

Today in the UK, land contaminated with pollutants is dealt with by two main approaches:

1. Part II(a) of the 1990 EPA (as amended) addresses contamination present on existing land uses; and
2. The Local Authority Planning System, which addresses contamination *via* land redevelopment.

Part 2A of the 1990 EPA (as amended) was introduced under Section 57 of the Environment Act 1995, and in this, the statutory definition of contaminated land is "*any land which appears to the local authority in whose area it is situated to be in such a condition, by reason of*

*substances in, on or under the land, that—*

*(a) significant harm is being caused or there is a significant possibility of such harm being caused; or*

*(b) significant pollution of controlled waters is being caused, or there is a significant possibility of such pollution being caused”.*

Through the 1990s, the common approach to assessing the human health risks from land contamination involved a simplistic approach of testing soil for ICRL listed contaminants and comparing soil concentrations with ICRL trigger values (1987). Some practitioners also derived in-house values or adopted international values such as Dutch- or USA-derived assessment criteria, but these values were not necessarily directly applicable in the UK. The ICRL trigger values (1987) were withdrawn in 2002 when the Environment Agency (EA) began the publication of Soil Guideline Values (SGVs). These are a key tool for generic assessment of health risks from land contamination. SGVs were derived using an exposure model called CLEA. SGVs now form part of a more comprehensive risk assessment framework, along with largely industry derived assessment criteria (published since 2002) for soil contaminants. Although significant progress has been made in contaminated land risk assessment since the withdrawal of ICRL trigger values, with the low number of SGVs produced and a current lull in the EA backed SGV programme, practitioners are reliant on generating their own assessment criteria and/or purchasing values derived by other organisations. The maintenance of a generally accepted risk assessment dataset for deriving generic assessment criteria is also a problem. Toxicity data and physiochemical and exposure parameters can be revised over time, and these changes will affect generic health risk assessments of land contamination.

Criteria used to assess surface water and groundwater contaminants are usually adopted from drinking water standards or Environmental Quality Standards for inland and coastal waters. Although many contaminants found in groundwater and surface water have an appropriate water quality standard, this dataset could be enlarged. Many common contaminants, e.g. total petroleum hydrocarbons, do not have a UK standard.

Today, the contaminated land risk assessment framework, which has developed over several decades,

helps to protect human health and the environment from soil and groundwater contamination. There is scope for improvement, but it can be argued that practitioners today conduct a far more comprehensive risk assessment of soil and groundwater contamination than twenty years ago.

*James Lymer*

## Air quality management

1995 was a pivotal year for air quality management in the UK, marking a transition from source-based to effects-based standards for managing ambient air quality. Part IV of the Environment Act 1995 set out the new legislative requirements for the Secretary of State, the Environment Agency and local authorities in relation to Local Air Quality Management (LAQM). Shortly after, the first National Air Quality Strategy (NAQS), published in March 1997, established health-based standards for eight air pollutants [benzene, 1,3-butadiene, carbon monoxide, lead, nitrogen dioxide, ozone, PM<sub>10</sub> (particulate matter with an aerodynamic diameter of 10 µm or less) and sulphur dioxide] based on advice from the Expert Panel on Air Quality Standards (EPAQS). These standards mirrored and were amended by EU air quality legislation in the form of Council Directive 96/62/EC and its subsequent daughter directives, later consolidated into Directive 2008/50/EC, to which Member States were required to adhere.

Whereas industry and agriculture still make a significant contribution to local air pollution in continental Europe, in the UK the main source is road traffic. Over the past twenty years, the greatest emissions reductions have been

for lead, sulphur dioxide and benzene, achieved through fuel quality standards imposed by the EU, which resulted in these pollutants being virtually eliminated from vehicle emissions by 2001. Possibly the most important factor in reductions of nitrogen dioxide and PM<sub>10</sub> has been the adoption of European vehicle emission standards (Euro standards). Between 1990 and 2011, UK NO<sub>x</sub> emissions reportedly fell by 64%, largely as a result of new fuel and engine technologies. However, recent evidence suggests that those NO<sub>x</sub> estimates may have been overstated by as much as 25%. In the past ten years, actual NO<sub>x</sub> and primary NO<sub>2</sub> emissions from Euro standard vehicle classes have not fallen by as much as test-track trials predicted. In addition, the greatest



*Air pollution. Credit : Cornfield/Shutterstock*



decreases in nitrogen dioxide expected with the latter Euro standards have been confounded by an increase in the proportion of primary NO<sub>2</sub> from diesel vehicles, effectively caused by the implementation of these technologies and by the climate change policy tax incentives that have ultimately led to the large growth in diesel vehicles in the UK.

At the same time, epidemiological studies have begun to reveal the breadth and severity of the health impacts of air pollution beyond previously recognised respiratory and cardiovascular effects. In October 2013, the World Health Organization's (WHO) International Agency for Research on Cancer (IARC) Working Group unanimously classified outdoor air pollution as carcinogenic to humans, and in 2014, a large scale cohort study in Europe (ESCAPE) identified a broad range of air pollution health effects. It has been estimated that in the UK, anthropogenic air pollution accounts for nearly 29,000 deaths annually (range 4,700 to 51,000 deaths) and may reduce birth-cohort life expectancy by an average of 1 to 12 months, presenting a greater mortality burden than passive smoking or road traffic accidents. These estimates are based on long-term exposure to fine particles (particulate matter with aerodynamic diameter below 2.5 µm, PM<sub>2.5</sub>) and therefore likely underestimate the cumulative impact of other pollutants (including NO<sub>2</sub>) and of short-term acute exposure. While PM<sub>2.5</sub> is regulated for Member States under Directive 2008/50/EC, it is not currently a requirement for UK local authorities under LAQM.

Although most regulatory goals for pollutants regulated under national and EU legislation have been achieved in the UK over the last twenty years, the health-based standards set for NO<sub>2</sub> are still widely exceeded in the UK, leading the European Commission to launch legal proceedings against the UK Government, on 20<sup>th</sup> February 2014, for "its failure to cut excessive levels of nitrogen dioxide". With the immediate 'low hanging fruit' of technological solutions already picked and rotted, in order to improve air quality and avoid EC fines, the UK government must now face some politically unpalatable alternatives, including reducing road traffic dependence as part of a more holistic, sustainable approach to air quality management.



Water pollution. Credit: Armograph/Shutterstock

## Water quality management

In the UK and worldwide, the field of water science has seen substantial changes over the past *ca.* twenty years. These changes are largely due to increasing awareness of water pollution and demands for water protection. This section will focus on three aspects related to the field of water environmental chemistry that have resulted in some of the biggest changes in the field: legislation, water monitoring methodology, and emerging contaminants.

In the past twenty years or so, changes to water regulations within the UK have been largely driven by EU legislation. These include the adoption of the Urban Waste Water Treatment Directive (1991), the Nitrates Directive (1991), the Directive for Integrated Pollution and Prevention Control (IPPC) (1996), the Drinking Water Directive (1998), the Groundwater Directive (2006), and the Marine Strategy Framework Directive (2008).

However, it is without doubt that the main influence in European water policy has been the introduction of the Water Framework Directive (WFD) in October 2000 and its transposition into UK national law through a series of regulations in 2003. The WFD encompasses most of the directives mentioned above. Unlike traditional limit value approaches to water pollution, the WFD does not set specific environmental quality standards and target limits. Rather, the directive focuses on means of achieving a 'good status' for all water bodies in terms of ecological and chemical considerations, without specifying target values. Additionally, it introduced the concept of water body management on the basis of river basins, some of which pass through several administrative and political borders.

The field of water monitoring has been driven not only by the implementation of these regulations, but also by substantial technological improvements in water sampling and analysis. Water sampling has seen a shift toward production control and pollution prevention through trend monitoring (as per the IPPC directive) and away from reactionary sampling following a pollution event or other cause for concern. An additional key shift has been toward automated sampling and online monitoring of water bodies, arising from

advances in such varied fields as microfluidics, electronics miniaturisation and wireless technologies. In addition to these technological advances, in recent years, the field of water monitoring has also seen some interesting shifts away from technological advances and into citizen science initiatives; for example, the OPAL water survey asks recreational anglers to report whether they have seen a specific type of fish.

There has also been an increasing focus on 'emerging contaminants', such as persistent organic pollutants (POPs), which were not on the agenda twenty years ago. This is evidenced, for example, by the adoption of the Stockholm Convention on POPs in 2001 (with implementation in the UK initiated in 2007) and the UK Water Industry Research (UKWIR) Chemicals Investigation Programme in 2009; the latter investigates trace contaminant concentrations in UK wastewater treatment works effluents and is now in its second phase. In addition to regulatory requirements, advances in mass spectrometric techniques, particularly tandem mass spectrometric and high resolution techniques, have undoubtedly been one of the main factors that have allowed this shift to occur.

*Cecilia Fenech and Ian Forber*

## Further reading

### Introduction

Some of these issues are discussed in a compendium of brief comment articles in *Nature*, **515**, 27-31 (2014) and pp. 32-33 (*ibid*) (E. B. Barber, *Account for the depreciation of natural capital*). For evocative descriptions of the same phenomena, I suggest *Wolf Totem* by Jiang Rong (translated by Howard Goldblatt, Penguin Press, 2008). *Engineers of the Soul* by Frank Westerman (translated by Sam Garrett, Vintage Books, 2010) discusses the impact of canal building in the 1950s on Turkmenistan and Kazakhstan. I also recommend *Rowing the Eternal Sea: the story of a Minamata fisherman* by Oiwa Keibo (narrated by Ogata Masato and translated by Karen Colligan-Taylor, Rowman and Littlefield Inc, 2001).

### Contaminated land

An overview of regulations regarding contaminated Land may be found at [www.york.gov.uk/info/200364/contaminated\\_land/490/contaminated\\_land](http://www.york.gov.uk/info/200364/contaminated_land/490/contaminated_land). Technical guidance is available at [www.gov.uk/government/collections/land-contamination-technical-guidance](http://www.gov.uk/government/collections/land-contamination-technical-guidance). For information on the USA perspective see [www.epa.gov/superfund/about.htm](http://www.epa.gov/superfund/about.htm).

For information on the Australian perspective see [www.public.health.wa.gov.au/3/1144/2/contaminated\\_sites.pm](http://www.public.health.wa.gov.au/3/1144/2/contaminated_sites.pm). The book *Assessment and Reclamation of Contaminated Land* (edited by R. M. Harrison, R. E. Hester and published by the RSC in 2001) covers topics from the origins and extent of contaminated land problems, including effects on human health, through investigative measures, to specific techniques of remediation.

### Air quality

Barnes, J. (2014) A critical evaluation of local air quality management and its contribution to meeting the EU annual mean nitrogen dioxide limit value. PhD, University of the West of England.

R. Beelen *et al.*, Effects of long-term exposure to air pollution on natural-cause mortality: an analysis of 22 European cohorts within the multicentre ESCAPE project. *Lancet*, **383**, 785 (2013).

S. D. Beevers, E. Westmoreland, M. C. de Jong, M. L. Williams, D. C. Carslaw, D.C. (2012) Trends in NO<sub>x</sub> and NO<sub>2</sub> emissions from road traffic in Great Britain, *Atmospheric Environment*, **54**, 107 (2012).

COMEAP (2010) The Mortality Effects of Long-Term Exposure to Particulate Air Pollution in the United Kingdom. Health Protection Agency. Environment Act 1995. Chapter 25. (1995) London: The Stationery Office.

J. W. S. Longhurst, J. G. Irwin, T. J. Chatterton, E. T. Hayes, N. S. Leksono, J. K. Symons, The development of effects-based air quality management regimes, *Atmospheric Environment*, **43**, 64 (2009).

### Water quality

Water Framework Directive Interactive Maps for Europe: <http://www.eea.europa.eu/themes/water/interactive/by-category/wfd>

Rapid Measurement Tools: ESKTN Business Case, <https://connect.innovateuk.org/documents/2832130/6075062/Rapid+Measurement+Tools.pdf/e0646f10-ef12-42eb-9477-8eae26341665>

European waters – current status and future challenges – a synthesis, EEA Report No 9/2012, <http://www.eea.europa.eu/publications/european-waters-synthesis-2012>

## Article

# Environmental chemistry degrees – then and now

Zoë Fleming (University of Leicester), Hattie Chisnall (University of Edinburgh) and Jashvini Jothieswaran (University of Edinburgh)

On the twentieth anniversary of the ECG *Bulletin*, Group member Zoë Fleming reflects on her experiences as an environmental chemistry student at the University of Edinburgh from the mid-1990s. Two current first-year students of environmental chemistry at the same University also discuss their experiences, motivations and hopes for the future.

## A student's reflections from twenty years ago

In the early 1990s, it seemed to me that humanity had finally admitted we were causing unnecessary harm to the environment. From a teenager's perspective, there was an incredible feeling of hope and a belief in the power to reverse this and join together to clean up our



Zoë Fleming assesses tree saplings for acid rain damage at CEH Edinburgh in the late 1990s.

act. As awareness of environmental issues grew, we talked our parents into recycling and buying eco-products, tried to plant a tree or two, and pestered our classmates to stop using aerosol deodorant sprays. We thought we could change the world. The 1992 Rio Earth summit became the focus of our hopes. My choice of degree was set upon reading James Lovelock's *The Ages of Gaia: A Biography of our Living Earth* and the realisation that chemistry was at the heart of this theory.

Environmental science degrees were growing in popularity in the 1990s, but degrees in environmental chemistry were only offered at two or three universities in the UK. When I began to study environmental chemistry at Edinburgh University in 1996, we were a tiny minority among the chemists we joined for most lecture courses and labs. In pursuing this degree I hoped to obtain the skills and chemical knowledge to fully understand any damage to the environment caused by humans and the chemical industry and to decipher the disturbance of the intricate balances in our water, soil and air.

Twenty years on, environmental chemists are less on the fringes of the key science questions. Today, we are needed to advise just about every industry. I am sure that environmental chemistry will continue to grow and play a key role in environmental protection, and that it will be taught within many other degree courses due to its interdisciplinary nature and broad relevance within environmental science.

*Zoë Fleming*

## Views of two first-year students today

Having grown up surrounded by the granite city of Aberdeen, the UK's biggest oil and gas merchant, many of my peers aspired to be a part of this booming industry, but this never really attracted me. Since deciding on a degree, I have realised that I want to be part of a progression into something cleaner, healthier and fresher: renewable energies. I want to do something that makes a difference and I see cleaner energy as an important factor in our progression to a cleaner planet.

My



*Hattie Chisnall in Edinburgh's Meadows*

generation has always lived with the pressure to “reuse, reduce and recycle”. Much has been achieved, but this generation can achieve much more. We know how serious the pressure on the Earth is now, and I, like many others my age, want to make a change.

I feel that there is a general optimism about environmental chemistry. A lot has been achieved, including a greater awareness of environmental issues among businesses, and building huge wind turbines all over the country. There is a lot of enthusiasm for change and environmental chemistry supports that enthusiasm. There seems to be more understanding about what environmental chemists can achieve now compared to twenty years ago, and there's still that enthusiasm but now we know how to go about it a bit more.

I really enjoyed chemistry at school. I had great teachers and also enjoyed reading about the subject and gaining a better understanding of how a lot of the world worked. I like my degree and feel like I have chosen the right one. It's been fun finding my feet at university so far. I do not know what job I want after University and I will probably leave that decision until my very last year. Right now it's just about getting a degree in something I really enjoy, whether it gives me my dream job or not.

**Hattie Chisnall**

I think environmental chemistry is an important aspect of chemistry. As scientists, we should be helping to find alternative ways to a more sustainable world. I find it interesting because it is a promising field in science as our non-renewable resources are starting to run low.

We only have one Earth and should be doing everything we can to safeguard it rather than destroy it. We do have better ways to synthesise the same products in a more environmentally friendly way. And sometimes the ‘greener’ way could actually also be more cost-effective. I



*Jashvini Jothieswaran enjoying Loch Ness*

studying environmental chemistry so I can help in some way to find better alternatives for a greener planet.

**Jashvini Jothieswaran**

## Courses for today's environmental chemists

A brief web survey of undergraduate degrees (apologies if I have left any out!) *via* [www.whatuni.com](http://www.whatuni.com) reveals environmental chemistry degree courses at Lancaster, Bangor, Aberdeen, York and Edinburgh, all with employment rates of between 81 and 90%.

As an environmental chemistry student who followed my degree with a chemistry PhD, I realised that there were many aspects of environmental science and management that were not included in my training. Knowledge of the interactions between earth, water, and atmospheric chemistry and our responsibility as environmental experts is not a given and must be built up from real world experience, reading up on the subject or further training.

When I was looking for work outside the academic sector a few years ago, I was told that a specialist Masters degree would be extremely helpful to an environmental science professional. There is a huge array of such Masters degrees, including Environmental, Analytical, Green, and Sustainable Chemistry titles as well as Pollution monitoring, Toxicological, Contaminated land, Environmental Assessment, Management, Policy, and Law among the *ca.* 700 advertised Environmental Masters degree courses at [www.findmasters.com](http://www.findmasters.com). There is no a shortage of degree courses for environmental chemists to choose from today – so no excuses now!

**Zoë Fleming**

### Forthcoming meeting

# New developments in the analysis of complex environmental matrices

The Royal Society of Chemistry Environmental Chemistry Group and the Separation Science Group are holding this joint meeting on Friday 6<sup>th</sup> February 2015 at the Science Suite, Royal Society of Chemistry, Burlington House, Piccadilly, London.

## Programme

- 9.00 Registration and coffee
- 9.50 Opening and welcome to meeting (Prof. Graham Mills, University of Portsmouth, Portsmouth)
- 10.00 Analysis of flame retardants in indoor dust and their metabolites in human liver cell lines by Orbitrap™-MS (Dr Mohamed Abdallah, University of Birmingham, Birmingham)
- 10.30 Use of metabolomics in solving environmental problems (Prof. Jake Bundy, Imperial College, London)
- 11.00 Coffee break
- 11.30 Monitoring of polar pollutants in surface waters using Chemcatcher-based passive sampling methods (Anthony Gravell, Natural Resources Wales, Llanelli Laboratory)
- 12.00 Analysis of marine biotoxins in shellfish (Dr Andrew Turner, CEFAS Weymouth Laboratory, Weymouth)
- 12.30 Pollution by polyisobutenes: a sticky problem for seabirds (Prof. Steve Rowland, University of Plymouth, Plymouth)
- 13.00 Lunch break and vendors' exhibition
- 14.15 Keynote lecture: LC tandem MS strategies for the analysis of contaminants of emerging concern in water, soil and sediment samples (Prof. Damia Barcelo, CSIC, Barcelona, Spain)
- 15.00 Aspect of drinking water quality – disinfection by products (Gavin Mills, Severn Trent Water Ltd.)
- 15.30 Screening for novel anti-androgenic contaminants in environmental samples using mass spectrometry combined with bio-assay procedures (Prof. Elizabeth Hill, University of Sussex, Sussex)
- 16.00 New developments in GC/MS and GC/PID instrumentation for rapid on-site analysis of trace environmental contaminants (Dr Andrew Hobson, Quantitech Ltd., Milton Keynes)
- 16.30 Meeting close (Dr Roger Reeve, University of Sunderland, Sunderland)

Members £90.00 (and of BMSS or Chromatographic Society, discount code BMCM22); non-members, £120.00; students, retired members, and the unwaged, £25.00

## Registration

<http://www.rsc.org/events/detail/12079/new-developments-in-the-analysis-of-complex-environmental-matrices>  
<http://www.rsc.org/Membership/Networking/InterestGroups/separationscience/ForthcomingEvents.asp>

## Contacts

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Dr Roger Reeve, University of Sunderland, Sunderland, UK (contact for late registrations)

Tel ++ 44 (0) 191 515 2596, [roger.reeve@sunderland.ac.uk](mailto:roger.reeve@sunderland.ac.uk)

## Update

# WMO Greenhouse Gas Bulletin No 10

The atmospheric concentrations of the main greenhouse gases – carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>), and nitrous oxide (N<sub>2</sub>O) – continued to rise in 2013 and were at 142%, 253%, and 121% of preindustrial levels (before 1750) by the end of 2013. This is one of the conclusions of the latest WMO Greenhouse Gas Bulletin, published on 9 September 2014 (1). Now in its tenth year, the Greenhouse Gas Bulletin reports global observations of long-lived greenhouse gases.

Carbon dioxide contributes around 65% to the overall radiative forcing by long-lived greenhouse gases (2). Between 2012 and 2013, the increase was the largest year-to-year increase in thirty years. The reasons for this larger-than-average increase remain unclear. The report concludes, however, that increased emissions from fossil fuel burning cannot explain the rise and that changes in the exchange of CO<sub>2</sub> between the atmosphere and the terrestrial biosphere from one year to the next provide a possible explanation.

The two other greenhouse gases that are discussed in detail are methane, which contributes 17% to the overall radiative forcing by long-lived greenhouse gases, and nitrous oxide, which contributes 6%. Both have anthropogenic as well as natural sources, although for methane, anthropogenic emissions currently exceed natural ones. Recent methane increases after a near-zero growth rate between 1999 and 2006 have continued in 2013 and are attributed to rising emissions from tropical wetlands and from mid-latitude anthropogenic sources.

Other greenhouse gases include the electrical insulator sulphur hexafluoride (SF<sub>6</sub>), an extremely potent greenhouse gas with a very long atmospheric lifetime. Although its contribution to greenhouse gas forcing is comparatively small, SF<sub>6</sub> data can help to evaluate the accuracy of emissions reporting and to validate chemical transport models. Finally, chlorofluorocarbon and related compounds contribute 12% to radiative forcing by long-lived greenhouse gases.

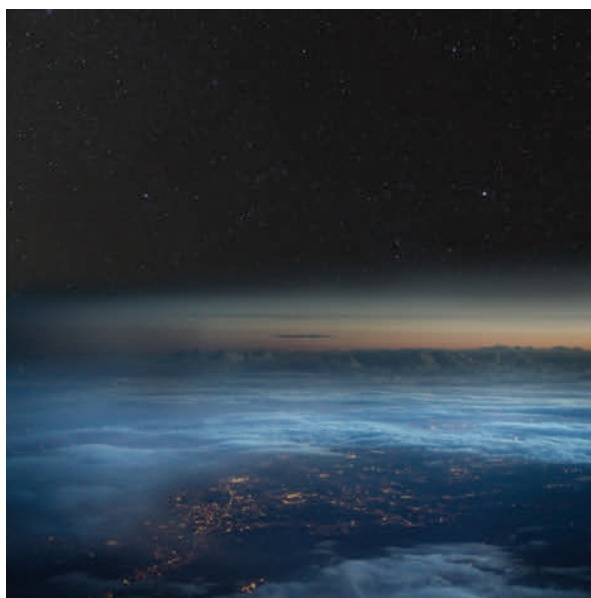
For the first time, the Greenhouse Gas Bulletin includes a section on ocean acidification. The ocean takes up around a quarter of anthropogenic emissions, measurably increasing the acidity of surface waters at measuring sites around the world's oceans. As a result, the ocean's capacity for taking up more carbon dioxide is reduced. The impacts of ocean acidification on marine organisms, particularly calcifying organisms, are likely to be complex and are not yet well understood. Only a few

marine stations currently conduct carbon dioxide measurements over long time scales, greatly limiting the ability to understand the impacts of carbon dioxide uptake on ocean chemistry.

## References

1. WMO Greenhouse Gas Bulletin (GHG Bulletin) No 10: The State of Greenhouse Gases in the Atmosphere Based on Global Observations through 2013, available at [library.wmo.int](http://library.wmo.int).
2. According to the IPCC, "Radiative forcing is a measure of the influence a factor has in altering the balance of incoming and outgoing energy in the Earth-atmosphere system and is an index of the importance of the factor as a potential climate change mechanism." Radiative forcing values typically refer to changes relative to preindustrial conditions at 1750. The units are Watts per square meter (W/m<sup>2</sup>). See: [http://www.ipcc.ch/pdf/assessment-report/ar4/syr/ar4\\_syr.pdf](http://www.ipcc.ch/pdf/assessment-report/ar4/syr/ar4_syr.pdf).

*The ECG Bulletin Editors*



*High altitude view of the Earth at night. As the latest WMO Greenhouse Gas Bulletin shows, greenhouse gas concentrations in the atmosphere continue to rise. The WMO publication also contains a section on ocean acidification as a result of rising atmospheric carbon dioxide concentrations. Credit: MarcelClemens/Shutterstock*

## Meeting report

# Chemical atmosphere–snow–sea ice interactions: taking the next big step in field, laboratory and modelling

Martin King (Royal Holloway, London, [m.king@rhul.ac.uk](mailto:m.king@rhul.ac.uk))

An AICI (Air-Ice Chemical Interaction, [www.igacproject.org/AICI](http://www.igacproject.org/AICI)) international workshop was held at Trinity Hall, Cambridge from 13 to 15 October 2014.

AICI is a subdivision of the Ocean–Atmosphere–Sea Ice–Snowpack (OASIS) program of IGAC (International Global Atmospheric Chemistry). Previous AICI workshops have produced influential state-of-science reviews. For example, a Special Issue in *Atmospheric Chemistry and Physics* ([www.atmos-chem-phys.net/special\\_issue275.html](http://www.atmos-chem-phys.net/special_issue275.html)) emerged from an AICI workshop held at Columbia University, USA in June 2011).

There were over 70 participants from over 15 countries at the three-day workshop, which followed on from a successful meeting in New York two years ago. The audience was mixed, with field/lab and modelling expertise from atmospheric, sea ice and snow scientists and biologists. The meeting was organised by the British Antarctic survey with an international organisation committee including the author. The purpose of the meeting was to review the current state of the science and produce a two-page report on the state of the science and how to move forward, for submission to *Science* or *Nature*.

The first two days of the meeting included reports on the influence of Arctic clouds (mixed phase) in the Arctic energy budget, laboratory studies exploring the interaction of ice with chemical constituents, the latest results from central Antarctica and Greenland field campaigns, and results from sea ice campaigns looking at halogen compounds coming from sea ice. There were reports from the new sea ice facilities, and about the complexities of light and sea ice and the different considerations needed for photochemistry, photobiology, and modern climate change. There was even some brief discussion of Martian astrobiology.

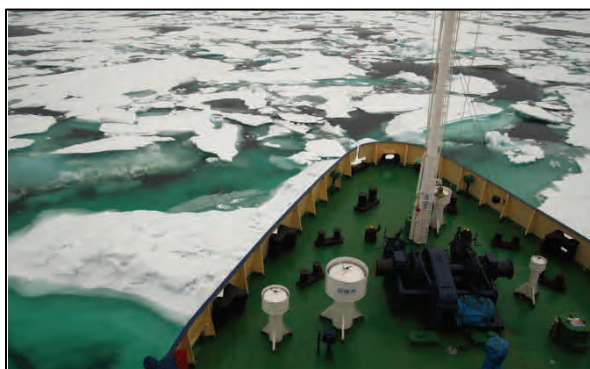
A substantial part of the workshop was spent in discussion and tutorials on new opportunities, including



*Icebergs in the glacier lagoon in Iceland Ekulsarlon. Credit: Sergemi/Shutterstock*

the creation of a new project in the Future Earth Programme (<http://www.icsu.org/future-earth>), and a very useful session on how to get large EU projects off the ground. In another session, station and ice breaker personnel reported on the capacities of their platforms and how to get on these platforms; this session was particularly important for those attempting to do science on the platforms of another country. The closer integration of modellers, laboratory scientist and field scientists was an important target as well.

Trinity Hall was a fantastic location for the workshop that included a tasty formal meal in Corpus Christi Hall, followed by beers in the infamous Eagle Pub.

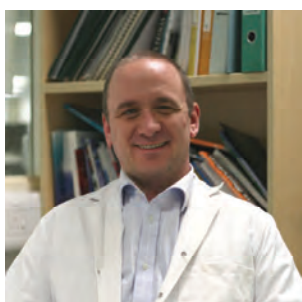


*A research vessel travels through sea ice in the Arctic. Credit: Kldy/Shutterstock*

## ECG Interview

# Ian Forber

ECG committee member Ian Forber is the Deputy Technical Manager at ALcontrol Laboratories (Hawarden) and the ECG's web pages co-ordinator. Here he tells us about his career as an environmental chemist.



### What inspired you to become a scientist?

I had an interest in and an aptitude for the sciences and mathematics at school. When I finished full time education I very nearly became a bank cashier. Instead I chose to work in a laboratory attached to a

metal refinery. As part of the job, I was sent to college on day release to study chemistry through the BTEC NC/HNC system and finally on to university. It was during this time that I realised that chemistry is a lot more interesting than banking.

### How did you come to specialise in inorganic analytical chemistry?

In my first job, we mostly analysed metals and metal residues. This suited me well as I have always been more interested in the areas of chemistry involving formulae and calculations with a precise result. My interest in the environmental aspects of chemistry developed from dealing with the Environment Agency following the introduction of Integrated Pollution Control (IPC) Regulations in the mid-1990s. When the opportunity came up to work as a technical specialist at ALcontrol, a laboratory specialising in environmental analysis, I jumped at the chance to work somewhere more closely involved in environmental concerns.

### Could you describe your current job?

ALcontrol is a multinational contract laboratory with over 60 laboratories across Europe. The laboratory I work for is the UK's contaminated land and non-potable waters division. As part of the technical team, I develop and validate new analytical methods, help to support and improve current methods used in routine production analysis, and resolve customer queries. The technical team also undertakes non-routine projects for customers,

giving us a chance to think creatively. As Deputy Technical Manager, I also support the Technical Director and cover for him when required.

### What advice would you give to anyone considering a career in environmental chemistry?

It can be a rewarding career if you have a genuine interest in the subject. Being truly interested will help you go further in any field and feel more fulfilled in your work. Environmental chemistry covers such a wide scope that I would suggest keeping your options open as you start your studies until you find an area that both suits and interests you.

### What are some of the challenges facing the environmental chemistry community?

From an analytical point of view there are always more compounds of environmental interest coming through that will usually need novel analysis methods. There is also constant pressure to lower limits of detection as regulations get tighter. For instance, the EU Water Framework Directive (WFD) looks for lower limits of detection for some compounds and different assessment approaches for other compounds.

Traditionally, analysis has aimed to determine the total amounts of compounds in the environment. Today, closer attention is paid to the impact levels of compounds and to which forms of particular compounds are most ecologically toxic. This requires, for example, speciation testing and measurement of bioaccessible levels in the environment. The resulting challenge for the environmental analytical community is to develop ever more complex analytical techniques.

### What is the most rewarding aspect of your career so far?

There have been several rewarding times in my career. One that comes to mind was a few years ago when I was asked to join the Environment Agency's Standing Committee of Analysts (SCA) to develop their 'Blue Book' standard method for the analysis of cyanides in soils.

### If you weren't a scientist what would you do?

I would probably have pursued a career in banking or accounting. I might have a better salary, but I am glad that I chose a career that challenges me on an almost daily basis.



## Article

# Veterinary agents and poisons threaten avian scavengers in Africa and Europe

Ngaio Richards (Working Dogs for Conservation, Three Forks, Montana, USA; [ngaio@workingdogsforconservation.org](mailto:ngaio@workingdogsforconservation.org)) and Darcy Ogada (The Peregrine Fund, Nairobi, Kenya; [darcyogada@yahoo.com](mailto:darcyogada@yahoo.com))

Perceived to be in competition with hunters and to prey on livestock, predators in Europe and Africa are deliberately poisoned *via* carcass baits laced with agricultural pesticides. As communal scavengers, vulture populations in these areas have been especially hard hit by the presence of poison-laced carcasses. Species that migrate between Europe and Africa face poisoning risks in either region. Residues of veterinary agents in the carcasses available to vultures, especially in Europe, are also of concern.

Europe has a long history of poisoning wildlife. In particular, predators that are in direct competition with hunters and may prey on livestock, are generally maligned. As communal scavengers, vultures have been hit particularly hard and have even been directly targeted because of the belief that they prey on young animals. Following severe declines of population in birds of prey (for example the Imperial Eagle, the Red Kite, and Cinereous and Egyptian Vultures), anti-poaching and anti-poisoning initiatives have been implemented in the EU over the past decade, but these problems nevertheless persist (1). In Africa, deliberate poisoning of wildlife has been documented for hundreds of years (2). When Africa's human population began to explode in the 1980s, the increasing need for agricultural and grazing lands exacerbated conflict between people and wildlife, especially carnivores (3). The commodification of Africa's natural resources also began in earnest around this time. All these factors led to an increase in



**Vultures under threat.** A Griffon vulture lands to join others at a feeding station. The vultures are under threat both from deliberate poisonings and because they are highly susceptible to veterinary agent diclofenac used in livestock. The image on page 18 shows Griffon vultures feeding on meat provided at the same station.

wildlife poisoning, particularly with agricultural pesticides, a practice that continues today (3). Added to these deliberate poisonings, there is a new threat from veterinary agents that are highly toxic to vultures. Thus, avian scavengers migrating between Europe and Africa face the prospect of poisoning in either region.

## Threats to vultures in Europe

In 2013, the nonsteroidal anti-inflammatory drug (NSAID) diclofenac, which nearly drove three *Gyps* vulture species to extinction in Asia (4), was registered for veterinary use in Spain, Italy, and several other EU countries (5, 6). Given that Spain is the main European vulture stronghold and that populations of some species

(such as the Egyptian and Bearded vultures) in Europe are faltering, the drug's presence on the veterinary market is perplexing and troubling. Sharma *et al.* (7) recently showed that diclofenac is also toxic to Steppe Eagles, raising additional concerns for Aquila eagles (such as the Imperial Eagle) and other avian scavengers.

Other NSAIDs (e.g. flunixin and ketoprofen) shown to be toxic to vultures and other birds (8) are

also registered for veterinary use in Europe (9). Residues of these and various other veterinary agents (e.g. antibiotics and euthanasia drugs) are therefore also potentially available to avian scavengers in livestock carcasses, whether at specially managed feeding stations, in captive/rehabilitation facilities, or in remote rural grazing areas where an affected animal cannot readily be retrieved after death. The potential repercussions of these other NSAIDs warrant further investigation (8, 9), but the relative threats (or lack thereof) in the European Union have not yet been established (10). And while the campaign against deliberate wildlife poisoning in Southern Spain is providing affected populations with temporary respite, this is still very far from resolved. A two-pronged response is still needed to address deliberate exposure to poisons and also non-deliberate exposure to veterinary agents.

## The situation in Africa

In Africa, deliberate wildlife poisoning has been implicated in population-level declines in large carnivores, raptors, and vultures, particularly in southern and East Africa (3). Scavenging species (e.g. lions, hyenas, jackals, vultures, and eagles) have been the

most impacted (3), with poisoning being the main driver in >60% of vulture declines over the past 30 years (11). During 2013, known vulture poisonings exceeded 2000 individuals—the highest figure to date and likely a gross underestimate, because most poisoning incidents are never reported (3, 11). The recent surge in elephant and rhino poaching using poisons and the associated poisoning of vultures likely represents one of the most important new threats to African vultures, one that is little reported even among conservationists.

There is also increasing concern about the use of veterinary diclofenac and other NSAIDs in livestock in Africa and their potential to harm African vultures (12), particularly in South Africa, where vulture 'restaurants' (feeding stations) are comparatively abundant and stocked primarily with the carcasses of dead livestock (13). Elsewhere on the continent, the NSAID threat to vultures is probably low because of (believed) minimal use of NSAIDs in livestock. Even where NSAIDs are used, the likelihood of vultures feeding on a treated carcass is small because dead livestock tends to be consumed by people (D. Ogada personal observation).

However, residues in domestic animals kept for transportation (e.g. horses, camels and donkeys) that may not be eaten upon death must still be verified.

## Exposure to veterinary agents versus deliberate poisoning

The term "poisoning" is now frequently (and, at least for the present time, misleadingly) used in conjunction with the exposure of vultures and other species to diclofenac. The drug is highly toxic to Old World vultures, which succumb to visceral gout after ingesting residues accumulated in the tissues of animals administered the drug during veterinary treatments. Other (often mammalian) scavengers appear to be far less susceptible to the drug. The key point is that any ensuing harm to vultures and other susceptible scavengers exposed to diclofenac-containing carcasses is unintentional. By contrast, in a "true" poisoning case, carcasses and other desirable food items (depending on the intended wildlife target) are intentionally laced with potent compounds such as strychnine, aldicarb, carbofuran, or chlorfenvinphos – anything that is readily available, highly effective, and inexpensive. All of these compounds are acutely toxic and indiscriminately kill any animal that



feeds on the bait.

The availability of potentially toxic veterinary drug residues in livestock carcasses and that of toxic compounds deliberately added to carcasses and other edible lures are, for now, two distinct threats, requiring different investigatory and remedial approaches. However, if would-be poisoners in European countries where diclofenac has been registered realize its potency to vultures, they may adopt it, or other available NSAIDs, as a poison. If this happens, the line between unintentional intoxication and deliberate poisoning will be blurred, and wildlife forensic investigations will have to be adapted accordingly. This concern should also be proactively extended to other veterinary agents that have been shown to harm scavengers feeding on previously treated livestock carcasses (15).

In both Europe and Africa, the deliberate poisoning menace to predatory and scavenging wildlife is particularly pressing, as several populations are being driven towards extinction. Local wildlife poisonings undermine national and international conservation efforts. The current surge in the use of poisons to poach elephants and rhinos is extremely worrying. The slightest additional threat, in this case in the form of available toxic residues of veterinary agents, can place an unsustainable strain on an already plummeting population. Concerted and sustained vigilance and monitoring of all veterinary agents known to be in use and potentially harmful is of utmost importance. Understanding the relative magnitude of, and inherent complexities presented by, each likely threat is essential to enacting stringent legal procedures and determining penalties in the ongoing battle to safeguard scavenging wildlife and the critical ecosystem balance they help maintain.

## Acknowledgements

We thank Jose Rafael Garrido, Alvaro Camiña, and Rafael Mateo for their feedback regarding the situation in Europe. We thank Iñigo Fajardo for providing the photographs of Griffon vultures at El Picacho Vulture feeding station, Cadiz Province, Andalucia, Spain. The feeding station is run for conservation purposes.

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7. A. K. Sharma *et al.* Diclofenac is toxic to the Steppe Eagle *Aquila nipalensis*: widening the diversity of raptors threatened by NSAID misuse in South Asia. *Bird Conservation International*, **24**, 282 (2014).
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### Forthcoming meeting

## Emerging contaminants in waters and soils, practical considerations: sampling, analysis and consequences

The RSC's Environmental Chemistry Group, Water Science Forum and International Network of Environmental Forensics Group will hold this joint meeting on 4 March 2015 at The Source Skills Academy, Sheffield, S9 1EA

### Programme

09:50	Registration and Refreshments
10:20	Welcome and Introduction, Kevin Prior, Chair, Water Science Forum
10:30	Rakesh Kanda, Brunel University
11:00	Graham Mills (and Anthony Gravell), Portsmouth University and Welsh EA
11:30	Maria Romero-Gonzalez <i>et al.</i> , University of Sheffield
12:00	Lunch and poster viewing
13:00	Marianne Stuart, British Geological Survey
13:30	Barbara Kasprzyk-Hordern, University of Bath
14:00	Zulin Zhang, James Hutton Institute
14:30	Refreshment break and poster viewing
15:00	Christine Switzer, University of Strathclyde
15:30	Simon Parsons – Winner of the RSC Sustainable Water Award for 2014
16:00	Discussion
16:30	Meeting closes

The organisers gratefully acknowledge the support of the Royal Society of Chemistry's Environment, Sustainability and Energy Division Council for sponsorship of the award to Professor Simon Parsons.

### Booking

<http://www.rsc.org/events/detail/16644/emerging-contaminants-in-waters-and-soils-practical-considerations-sampling-analysis-and-consequences>

<https://www.eventbrite.co.uk/e/emerging-contaminants-in-waters-and-soils-practical-considerations-sampling-analysis-and-tickets-13548480871>

### Organizing committee

Kevin Prior	RSC Water Science Forum
James Lymer	RSC Environmental Chemistry Group and Wardell Armstrong Sheffield
Clive Thompson	RSC Water Science Forum and Alcontrol
Richard Allan	RSC Water Science Forum and Cobalt Solutions
Stephen Mudge	International Network of Environmental Forensics and Exponent

### Contact for further details

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# Atmospheric lifetimes of trace gases

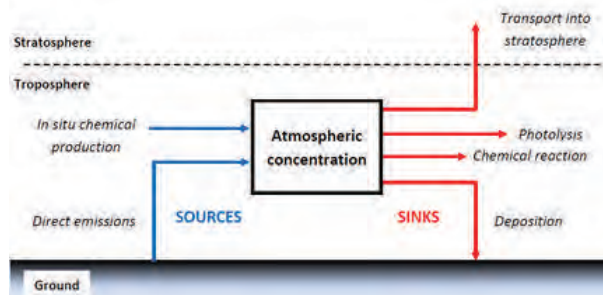
Stephen Ball (Department of Chemistry, University of Leicester, sb263@leicester.ac.uk)

The atmospheric concentration of a trace gas is determined by the balance between its sources and sinks. However, the sink processes alone determine the lifetime (residence time) of the gas in the atmosphere. This Environmental Brief outlines how lifetimes are calculated and presents some caveats about their interpretation.

Many trace gases are emitted directly into the atmosphere (**Figure 1**). Examples for these primary emissions include nitrogen oxides ( $\text{NO}_x = \text{NO} + \text{NO}_2$ ) from fossil fuel combustion and vehicle exhausts, and hydrocarbons of both biogenic and man-made origin. Primary emissions generally enter the atmosphere from sources located on the Earth's surface, and so this Brief concentrates on tropospheric chemistry. A second subset of trace gases is generated *in situ* by chemical and photochemical processes within the atmosphere: for example, tropospheric ozone is a secondary pollutant. Trace gases are removed by various sink processes. Reactive species (such as ozone) or soluble species (such as nitric acid) are deposited by contact with the ground; carbon dioxide is taken up by plants. A few chemically important molecules (notably ozone and  $\text{NO}_2$ ) undergo photolysis in the troposphere (1). However, the main sink for most trace gases is reaction with a tropospheric oxidant such as OH or  $\text{NO}_3$  radicals (1, 2). Only those compounds that do not photolyse and do not react with tropospheric oxidants (or do so only slowly) persist long enough to be transported into the stratosphere, chlorofluorocarbons being pertinent examples.

## Lifetimes

To understand the concept of a lifetime, consider a trace gas that is removed from the atmosphere *via* a single sink process characterised by a first-order rate coefficient  $k$  (with units 1/time). Suppose also that the sink balances



**Figure 1:** A summary of atmospheric sources and sinks. Note that this particular model neglects physical transport of trace gases into and out of the central box.

the sources of this trace gas, so its concentration is stable (**Figure 2**). Next, suppose that an instantaneous, extra pulse of the trace gas ( $P_0$ ) enters the atmosphere: this occurs at Year 2 in **Figure 2**. The amount of extra gas is so small that it does not perturb other atmospheric processes. After the pulse, the excess concentration  $P$  decays exponentially with time as the concentration of the trace gas re-establishes steady-state:

$$P = P_0 \exp(-kt) \quad (\text{eq. 1})$$

Recasting eq. 1 in terms of a decay time  $t$  gives

$$P = P_0 \exp(-t/\tau) \quad (\text{eq. 2})$$

Thus the atmospheric lifetime of the gas is the inverse of the first-order rate coefficient for its sink process:

$$\tau = 1/k \quad (\text{eq. 3})$$

**Figure 2** illustrates another important result. The amount of extra gas emitted is the same in the two cases shown, but whereas the short-lived gas essentially re-establishes its steady-state concentration within five years of the emission event, the effects of the long-lived gas persist for decades. It is no coincidence that the major greenhouse gases ( $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{N}_2\text{O}$ ) implicated in anthropogenic climate change are long-lived.

The same concept can be applied to a trace gas with multiple sinks, except now the rate coefficient is the sum of the first order rate coefficients characterising each of the various sink processes, as given in eq. 4. By analogy with eq. 3, the overall atmospheric lifetime is given by the reciprocal of the sum of the reciprocal lifetimes for each sink process (eq. 5). Note that the overall lifetime is necessarily shorter than even the shortest lifetime

characterising the fastest sink process.

$$K_{\text{total}} = k_1 + k_2 + k_3 + \dots \quad (\text{eq. 4})$$

$$1/\tau_{\text{total}} = 1/\tau_1 + 1/\tau_2 + 1/\tau_3 + \dots \quad (\text{eq. 5})$$

For example, methyl chloroform ( $\text{CH}_3\text{CCl}_3$ ) has lifetimes of 6.0 years for loss by reaction with OH, 38 years for loss into the stratosphere and 94 years for deposition to the ocean (3).  $1/\tau_{\text{total}} = 1/6.0 + 1/38 + 1/94 = 0.204 \text{ year}^{-1}$  and so the overall lifetime is  $\tau_{\text{total}} = 1/0.204 = 4.9$  years.

## Chemical loss

The rate-limiting step in the atmospheric degradation of very many trace gases is their reaction with OH radicals during the day. The lifetime of a trace gas A with respect to reaction with OH is

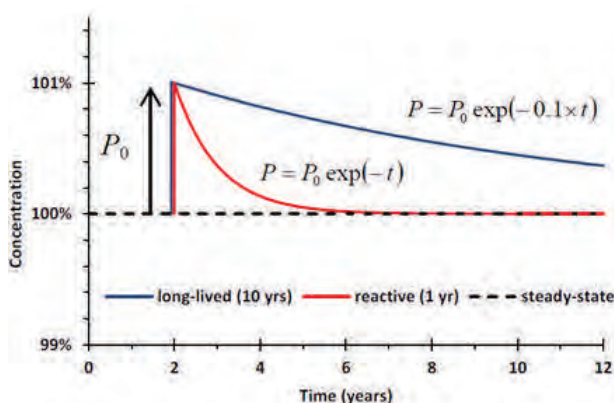
$$\tau_{\text{OH}} = 1/(k_{\text{OH}} \times [\text{OH}]) \quad (\text{eq. 6})$$

where  $k_{\text{OH}}$  is the rate coefficient for the second-order reaction  $\text{A} + \text{OH} \rightarrow \text{products}$  and  $[\text{OH}]$  is the atmospheric concentration of OH radicals. An analogous expression provides the lifetime for oxidation by  $\text{NO}_3$  radicals at night. Reaction with ozone and chlorine atoms can also sometimes initiate oxidation of trace gases.

For example, OH reacts with isoprene (emitted by plants) with a rate coefficient  $k_{\text{OH}} = 1.0 \times 10^{-10} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$  at 298 K (4). Assuming an average  $[\text{OH}]$  of  $2 \times 10^6 \text{ molecules cm}^{-3}$  during daylight (= 12 hours), eq. 6 yields  $\tau_{\text{OH}} = 1.4$  hours. Note here  $\tau_{\text{OH}}$  is the day-time lifetime of isoprene's loss *via* OH: at night,  $[\text{OH}]$  is zero and  $\tau_{\text{OH}}$  is thus indefinite. Isoprene also reacts with  $\text{NO}_3$  ( $k_{\text{NO}_3} = 7.0 \times 10^{-13} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$  at 298 K (4)). Eq. 6 gives  $\tau_{\text{NO}_3} = 0.8$  hours assuming  $[\text{NO}_3] = 5.0 \times 10^8 \text{ molecules cm}^{-3}$  at night (= 12 hours). Since  $[\text{NO}_3]$  is zero in daylight (2),  $\tau_{\text{NO}_3}$  is indefinite during the day. The mean lifetime of isoprene over the 24-hour diurnal cycle is  $\approx 1.1$  hours.

## Caveats

The simple analysis outlined above has some problems. In particular, eq. 6 predicts the lifetime of methane to be 5.0 years using  $k_{\text{OH}} = 6.4 \times 10^{-15} \text{ molecules}^{-1} \text{ cm}^3 \text{ s}^{-1}$  at 298 K (4) and a representative 24-hour average of  $[\text{OH}] = 1 \times 10^6 \text{ molecules cm}^{-3}$ . (Methane does not react with  $\text{NO}_3$ ). However, methane's lifetime for OH oxidation is widely accepted to be a factor of two longer: e.g. 9.7 years (5). The discrepancy arises in part from having used the 298 K rate coefficient in eq. 6. Reactions of OH or  $\text{NO}_3$  with hydrocarbons have an activation energy barrier, and hence the rate coefficients decrease with decreasing temperature (4). Outside of equatorial regions and summertime temperate regions, temperatures are below 298 K and methane's lifetime is



**Figure 2:** Concentration-time profiles for gases with lifetimes of 1 and 10 years.

correspondingly longer. Vertical mixing of methane to higher and hence cooler altitudes also considerably prolongs its lifetime (5).

Another major issue concerns what OH concentration to use in eq. 6. OH concentrations peak around midday and tail off to zero at sunrise and sunset; the assumption of a constant mean OH concentration is a gross simplification. OH concentrations also vary with the seasons due to the differences in solar zenith angles and the number of hours of daylight. In practice, methane's atmospheric lifetime is negligibly influenced by diurnal and seasonal variations in OH because methane is sufficiently long-lived for these effects to average out (5), but such OH variations are important for shorter-lived species. Methane's lifetime instead depends on latitudinal variations in OH, and equatorial regions have the highest OH concentrations. These factors, allied to the temperature dependence of the  $\text{OH} + \text{CH}_4$  reaction rate, result in 60% of global methane being oxidised between  $30^\circ\text{S}$  and  $30^\circ\text{N}$  at altitudes between the ground and 5 km (5). The global atmospheric lifetime of methane is best estimated from a weighted average of methane lifetimes calculated over different latitudes and altitudes.

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# How do passive diffusion tubes measure $\text{NO}_2$ concentrations?

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As part of the UK Air Quality Strategy, Local Authorities are legally obliged to assess atmospheric  $\text{NO}_2$  concentrations (and those of other specified air pollutants). The best method for measuring ambient  $\text{NO}_2$  concentrations is the chemiluminescence analyser, providing real-time data at high precision. However, the analysers are expensive and need power and security at the operating site. Local Authorities therefore continue to take advantage of the simplicity and low cost of passive diffusion tubes (PDTs) to assess  $\text{NO}_2$  concentrations across a spatial network. This Brief explains how PDTs work and describes some of their limitations.

## Principles of PDT methodology

The passive samplers used in the UK are of the tube design first introduced by Palmes *et al.* in 1976 (1) (Figure 1). They consist of 7.1 cm-long acrylic plastic tubes, with an internal cross-section of  $0.92 \text{ cm}^2$ , with the  $\text{NO}_2$  absorbent triethanolamine [ $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$ , TEA] coated onto two stainless steel grids in the internal end. TEA is assumed to be 100% efficient at facilitating the 1:1 conversion of  $\text{NO}_2$  molecules into nitrite ( $\text{NO}_2^-$ )

anions.

Samplers are typically exposed just above adult breathing height, with the open end of the tube facing downward (to avoid rain ingress) for a period of 1-4 weeks. At the end of the exposure the tubes are recapped. The nitrite in the TEA is subsequently extracted in the laboratory into a known volume of water and quantified either directly by ion chromatography or by a colorimetric procedure. The latter involves adding solutions of sulphanilamide and *N*-(1-naphthyl) ethylenediamine (NEDA) to form a pink dye; the absorbance intensity of this dye (measured at a wavelength of 540 nm) is proportional to the nitrite concentration in the extracted solution and hence to the amount of  $\text{NO}_2$  captured by the sampler during exposure.

The PDT operates through the diffusion of  $\text{NO}_2$  molecules down the concentration gradient set up between the concentration in the ambient air at the mouth of the tube and the TEA absorbent. Assuming zero  $\text{NO}_2$  concentration in the air just above the absorbent, the concentration gradient is  $-\text{NO}_2]_{\text{av}}/L$ , where  $[\text{NO}_2]_{\text{av}}$  is the average concentration at the mouth of the tube during exposure and  $L$  is the length of the tube. For an exposure duration  $t$ , the total amount,  $Q$ , of  $\text{NO}_2$  collected (as  $\text{NO}_2^-$ )

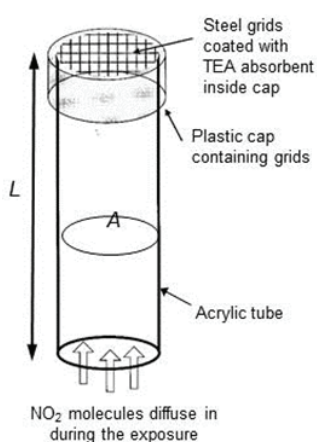


Figure 1: Schematic of a Palmes-type passive diffusion tube, and an example deployment (photo from Gradko International Ltd.).

is given by:

$$Q = [\text{NO}_2]_{\text{av}} ADt/L \quad (\text{eq. 1})$$

where  $A$  is the internal cross-sectional area of the tube and  $D$  is the diffusion coefficient for  $\text{NO}_2$  in air. Rearranging gives the expression for the average  $\text{NO}_2$  concentration during exposure as:

$$[\text{NO}_2]_{\text{av}} = QL/ADt \quad (\text{eq. 2})$$

The value of  $D$  recommended by the UK working group convened on behalf of Defra to report on harmonisation of  $\text{NO}_2$  passive diffusion tube (PDT) procedures is  $0.151 \text{ cm}^2 \text{ s}^{-1}$  (2).

## Limitations of PDT performance

The inherent simplicity of the PDT method means that its precision and accuracy cannot in general compare with that of a chemiluminescence analyser. A number of factors may influence both precision and accuracy of  $\text{NO}_2$  concentrations derived from PDT data (2, 3). Factors that may influence  $\text{NO}_2$  PDT performance include the following, at different stages of a PDT measurement:

1. In PDT preparation: the mass of TEA applied to the grid; the choice of solvent (water or acetone) used to apply TEA absorbent to the grids; and whether the TEA is applied by dipping grids in the TEA:solvent solution or by pipetting the solution directly onto the grids.
2. In PDT exposure: humidity and temperature of the ambient environment; air turbulence at the mouth of the tube during exposure (which can shorten the effective diffusion path length, leading to systematic positive bias in the  $\text{NO}_2$  concentration); production of additional  $\text{NO}_2$  in the tube by reaction of co-diffusing  $\text{NO}$  and  $\text{O}_3$  (a consequence of the opacity of the standard acrylic tubes to  $\text{NO}_2$  photolysis wavelengths), again leading to systematic positive bias (4); and degradation of the nitrite-TEA complex during exposure, leading to systematic negative bias.
3. In PDT analysis: the concentration of the colorimetric reagents; and degradation of the dye between its formation and the measurement of its absorption.

The  $\text{NO}_2$  PDT harmonisation working group recommended specific protocols regarding many of the above issues (2). For example, absorbent preparation should be done either by dipping grids in 50:50 TEA:acetone solution or by pipetting 50  $\mu\text{L}$  of 20:80 TEA:water solution onto the grids.

Some effects of temperature and relative humidity on PDT performance have been noted but these have been variable and within the general uncertainties in PDT measurements.

The two major lingering bias concerns for PDTs are the positive biases from within-tube chemical production of additional  $\text{NO}_2$  and the effect of air movement across the mouth of the tube causing a shortening of the diffusion path compared with the physical length of the tube.

The magnitude of the former bias depends on the relative amounts of  $\text{NO}$ ,  $\text{NO}_2$ , and  $\text{O}_3$  in the ambient air and will be greatest when  $\text{NO}$  and  $\text{O}_3$  concentrations are both comparable to  $\text{NO}_2$  concentrations. This means that the effect is likely to be most significant in urban background areas, and not at road sides, where  $\text{O}_3$  concentrations tend to be low, nor in rural areas, where most  $\text{NO}_x$  is already in the form of  $\text{NO}_2$ .

Average positive biases of the order of 10 to 20% have been reported for PDT exposures in urban background air. The wind-induced bias will clearly be highly dependent on the nature of the deployment site and of the windiness during a given exposure. The use of shelters over the PDT or a coarse mesh across the "open" end of the tube during exposure may be able to mitigate against this positive bias, although further research on this particular issue is necessary.

The EU Directive on air quality (5) recognises the uncertainties in  $\text{NO}_2$  passive samplers and designates them as indicative measures of  $\text{NO}_2$  with a potential uncertainty of  $\pm 30\%$ . Overall, however, with careful preparation and analysis, coupled with an appreciation of issues of potential limitation,  $\text{NO}_2$  PDTs remain a very useful method for understanding spatial and longer-term trends in ambient  $\text{NO}_2$  concentrations.

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